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by

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Synthesis of Oligomeric Anilines

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Abstract

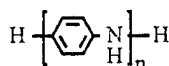
Parent aniline oligomers such as tetramer and "16-mer" have been synthesized by a general method. This method can be used to synthesize other oligomers by selecting appropriate ratios of reactants and appropriate oxidants. The oligomers were characterized by UV/Vis, IR, NMR, mass spectroscopy, GPC and elemental analysis. The conductivities of HCl doped oligomers were lower than that of polyaniline.

Keywords: Polyaniline and derivatives; Coupling reactions; Elemental analysis; Infrared spectroscopy; UV-Vis-NIR

1. Introduction

Although polyaniline was discovered about ~150 years ago, it was realized only recently that polyaniline could be a conductive polymer after doping. Because of convenience of synthesis and excellent stability in air, polyaniline has become one of the most studied polymers in conducting polymer field. However, polyaniline oligomers have attracted less attention. A polyaniline tetramer called azurin was reported in 1907 without comprehensive analyses [1]. In 1968, J. Honzl [2] had studied a series of oligoaniline derivatives. Based on a modified Honzl approach, Wudl et al, [3] synthesized a phenyl-capped octamer which was reported to have essentially the same properties as polyaniline.

Polyaniline oligomers may be end-capped with a combination of a variety of groups such as phenyl, amine, etc. [4]. We have been particularly interested in oligomers of the type



represented for simplicity in its completely reduced form, capped with a phenyl group at one end and an amine at the other. In this study, we present a general, simple method for the synthesis of parent polyaniline oligomers such as tetramer, octamer and "16-mer" in aqueous solution by oxidative coupling reactions.

2. Experimental

All chemicals were used as received. The hydrochloride salt of N-phenyl-1,4-phenylenediamine (98%), anhydrous hydrazine (98%) were from Aldrich. Ammonium peroxydisulfate (98%), ferric chloride hexahydrate (99%), ammonium hydroxide (30%), hydrochloric acid (37%), carbon (decolorizing DARCO G-60), ethyl ether (99%), ethanol (95%) and N,N'-dimethylformamide (DMF, 99%) were from Fisher.

Vacuum filtration was carried out with a Buchner funnel with #4 Whatman filter paper by using a water aspirator.

2.1. Synthesis of Tetramer

Ferric chloride hexahydrate (0.1mole) was dissolved in 100ml 0.1M HCl at room temperature. The hydrochloride salt of N-phenyl-1,4-phenylenediamine (dimer, 0.1mole) was suspended in 500ml 0.1M HCl in a 2000ml beaker with strong *mechanical* stirring for 0.5 hour at room temperature. The ferric chloride solution was added to the dimer suspension, with strong stirring, *very quickly*. The suspension was then remained stirring for 2 hours.

After 2 hours, the suspension was filtered by vacuum filtration. The collected precipitate was transferred into a 500ml of 0.1M HCl. The resulting suspension was stirred for 1 hour, and filtered through the same Buchner funnel. This washing process was repeated 5 times. Alternatively, the precipitate could be separated and washed by centrifugation.

The precipitate was dedoped by 0.1M ammonia hydroxide. The precipitate was dried in dynamic vacuum for 24 hours at room temperature.

A typical elemental analysis for C₂₄H₂₀N₄ was: Found, C, 78.81, H, 5.60, N, 15.27. Calcd, C, 79.10, H, 5.53, N, 15.37. Its mass spectrum showed a molecular ion peak at 365 (MH⁺/e) by chemical ionization. Its molecular weight by GPC was 374. UV/Vis and IR spectra are given in Figures 1 and 2, respectively. It is concluded from these spectra that the as synthesized tetramer, after conversion to their base form by NH₄OH, is in the emeraldine oxidation state.

The tetramer powder in the emeraldine oxidation state was suspended in 500ml 1M HCl for 24 hours at room temperature. The doped powder was collected by vacuum filtration and was dried under dynamic vacuum for 20 hours at room temperature. The conductivity of the HCl-doped tetramer was 3.0x10⁻³ S/cm (compressed pellet, 4 probe).

The tetramer was reduced to the leucoemeraldine oxidation state by refluxing with anhydrous hydrazine in ethanol. After filtration, the powder was recrystallized from ethanol.

A typical elemental analysis for $C_{24}H_{22}N_4$ was: Found, C, 78.38, H, 6.02, N, 15.28. Calcd, C, 78.67, H, 6.05, N, 15.29. The mass spectrum showed a molecular ion peak at 367 (MH^+) by chemical ionization. The IR spectrum is shown in Figure 2. 1H NMR (DMSO): 7.7(s,1), 7.5(s,1), 7.2(s,1), 7.1(t,2), 6.8(m,12), 6.6(t,1), 6.5(d,2) and 4.6(s,2). ^{13}C NMR (DMSO): 145.7, 142.6, 139.9, 139.8, 135.1, 134.1, 133.5, 129.0, 121.0, 120.5, 119.6, 117.7, 116.3, 115.9, 114.9 and 114.4

2.2 Synthesis of "16-mer"

Ammonium peroxydisulfate (0.015mole) was dissolved in 50ml of 0.1M HCl solution at room temperature. The tetramer in the leucoemeraldine oxidation state (0.01mole) was suspended in 200ml 0.1M HCl solution with magnetic stirring for 0.5 hour at room temperature. The ammonium peroxydisulfate solution was added *very quickly* into the tetramer suspension with vigorous stirring. After 2 hours, the reaction mixture was collected, washed and dedoped following the method given in section 2.1. The dried powder (mixture of "16-mer", octamer and tetramer) was extracted with 150ml ethyl ether by using a Soxhlet extractor. The insoluble powder remaining in the thimble was the "16-mer". It was held in a desiccator under dynamic vacuum for 24 hours before characterization.

The mass spectrum showed a parent ion at 1451 (MH^+) by laser desorption ionization. Molecular weight by GPC was 1486. UV/Vis and IR spectra were shown in Figs 1 and 2. It is concluded from these spectra that the as synthesized "16-mer", after conversion to their base form by NH_4OH , is in the emeraldine oxidation state.

The "16-mer" powder in the emeraldine oxidation state (0.5g) was suspended in 200ml 1M HCl for 24 hours at room temperature. The doped powder was collected by vacuum filtration and was dried under dynamic vacuum for 24 hours at room temperature. The conductivity of HCl doped "16-mer" was 4.0×10^{-3} S/cm (compressed pellet, 4 probe).

The "16-mer" in the leucoemeraldine oxidation state was synthesized by refluxing the "16-mer" powder in ethanol/DMF mixed solvent (4:1 v/v) with anhydrous hydrazine. The collected powder was recrystallized from ethanol/DMF. The gray white powder was collected by vacuum filtration and was dried under dynamic vacuum for 12 hours.

A typical elemental analysis for $C_{96}H_{82}N_{16}$ was: Found, C, 78.90, H, 5.74, N, 13.47, total, 98.11. Calcd, C, 78.99, H, 5.66, 15.35.

3. Discussion

It is interesting to find that the peak position of the exciton absorption is 610nm for the "16-mer" in NMP solution, which is between 590nm for the tetramer and 638nm for polyaniline (EB) in the same solvent as shown in Figure 1. Although the ratio of $\pi-\pi^*$ transition to exciton transition for the "16-mer" is about 1.5 compared to ~ 1.0 for polyaniline, it is understood that there are fewer exciton units than $\pi-\pi^*$ transition units in the "16-mer" compared to polyaniline because of end group effects. For the "16-mer" in the emeraldine oxidation state, the end group is quinoid imine which is not a complete exciton chromophore. This structure is

also consistent with the 1H NMR spectrum since there is no NH_2 signal.

The aniline oligomers discussed offer the opportunity of directly studying the relative importance of *intra*-molecular and *inter*-molecular contributions to the bulk conductivity of polyaniline.

4. Conclusion

A general method is described for synthesis of parent oligomers of polyaniline in aqueous solution by oxidative coupling reactions. The tetramer and "16-mer" were well characterized. The conductivities of the doped tetramer and 16-mer were 3 orders of magnitude lower than that of doped polyaniline.

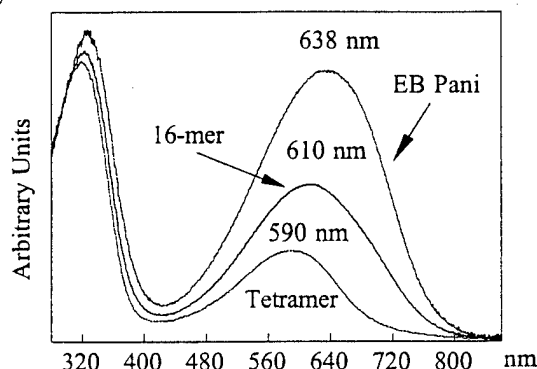


Figure 1. UV/Vis spectra of polyaniline (emeraldine base), "16-mer" and tetramer in NMP solution

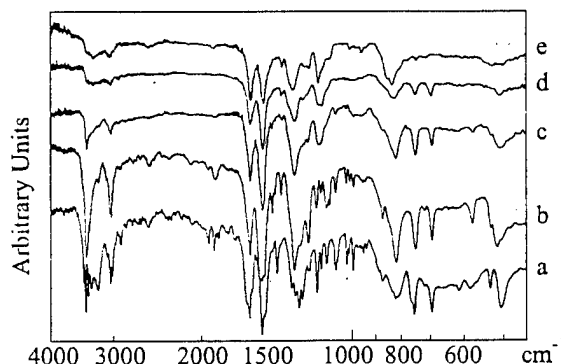


Figure 2. Diffuse reflectance FTIR of: a, leucoemeraldine dimer; b, leucoemeraldine tetramer; c, emeraldine tetramer; d, emeraldine "16-mer"; e, polyaniline (emeraldine base)

Acknowledgments

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